



Effective catalysts for the low-temperature NH₃-SCR process based on MCM-41 modified with copper by template ion-exchange (TIE) method

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ABSTRACT

Effective catalysts for the low-temperature process of selective catalytic reduction of NO with ammonia (NH₃-SCR) were obtained by deposition of copper species on MCM-41 using template ion-exchange method (TIE). It was shown that the form and aggregation of deposited copper species depend on concentration of copper salt (CuCl₂) solution and solvent composition used for TIE procedure. In the case of methanol solution of CuCl₂ copper in the highly dispersed form, mainly monomeric species, was deposited on the silica support, while in the case of water containing solutions of CuCl₂ more aggregated CuO species were formed. The efficiency in deposition of highly dispersed copper species was significantly improved by treatment of the MCM-41 samples with ammonia directly after TIE procedure. In this case nearly 13 wt.% of copper was deposited on MCM-41 nearly exclusively in the form of monomeric cations. The catalysts obtained by this method presented high activity, selectivity to N₂ and stability in the low-temperature (200–300 °C) NH₃-SCR process.

1. Introduction

Nitrogen oxides (NO_x) are formed mainly as side-products of fossil fuels combustion in power plants, vehicles and factories. NO_x cause a series of environmental issues such as photochemical smog, acid rain, ozone depletion and also contribute in the global warming problem [1,2]. These environmental problems have stimulated development of various technologies for abatements of NO_x emission [3]. There are three main groups of such technologies: (1) minimizing the nitrogen content in the fuels before the combustion process, e.g. hydrodenitrification process, to limit the formation of *fuel* NO_x; (2) controlling the combustion process mainly by decreasing combustion temperature, e.g. exhaust gas recirculation system, to limit the formation of *thermal* NO_x; (3) post-combustion technologies used for elimination of NO_x from flue gases, e.g. selective catalytic reduction of NO_x with ammonia (NH₃-SCR).

The NH₃-SCR, which is currently the most important post-combustion technology for NO_x abatement, is based on the selective reduction of NO_x with ammonia to dinitrogen and water vapour in the presence of catalysts. The NH₃-SCR technology was firstly applied in Japan in the 1970's and then has been installed in the USA, Europe and several Asian countries [4]. The major industrial catalyst for this process is based on V₂O₅-WO₃/TiO₂ metal oxide system, which effectively operates in a

relatively narrow temperature window of 300–400 °C [4–6]. At temperatures below 300 °C, the activity is too low and therefore the efficiency of the NH₃-SCR process is not satisfying, while at temperatures above 400 °C the side process of direct ammonia oxidation by oxygen, resulting in NO and N₂O, limits the application of these catalytic systems. Typically NH₃-SCR catalyst, in the form of monolith, is located upstream of electrostatic precipitator (ESP) and therefore operates with dusty gas stream (high-dust SCR). Particles of dust may clog channels in the monolith and deactivate catalytic system. In order to avoid such problem the monolithic NH₃-SCR catalyst could be located downstream of ESP unit (low-dust SCR). However, temperatures of flue gases downstream of EPS are about 250 °C or even lower [7]. Therefore, for such low-dust SCR process effective catalysts operating below 250 °C are necessary. Among the most promising catalysts for the low-temperature NH₃-SCR process are transition metals (Cu, Cr, Mn) deposited on TiO₂, which were reported to be catalytically active at temperatures above 120 °C [8,9], however at higher temperatures (> 200 °C) efficiency of NO_x conversion decreased due to the side process of direct ammonia oxidation by oxygen present in the reaction mixture [9]. Various zeolites modified with copper were reported to be active and selective catalysts of NH₃-SCR [10–14]. Martin et al. [15] reported high catalytic activity of high-silica SSZ-39 zeolite modified with copper in the NH₃-SCR process. It was shown that NO conversion of nearly 100%

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was obtained at 250 °C with a very high selectivity to dinitrogen. It seems that low-temperature activity of the studied catalysts is strongly related to the presence of copper in the form of highly dispersed species, mainly monomeric copper cations stabilized by the zeolite framework. Akter et al. [16] studied chabazite (CHA) modified with copper by impregnation method as catalyst for NH₃-SCR. It was shown that an increase in copper loading to about 5 wt.% resulted in a gradual increase in catalytic activity, while deposition of larger amount of copper caused a decrease in NH₃-SCR efficiency due to the side process of direct ammonia oxidation by oxygen present in the reaction mixture. For the best catalysts the high NO conversion (> 80%) was obtained at temperature 200 °C. The activity in low-temperature NH₃-SCR was attributed to the presence of copper in the form of highly dispersed species. Thus, the nature of deposited copper species is very important for preparation of active and selective catalyst for NH₃-SCR [17–22].

Mesoporous silica materials are very promising as catalytic supports due to a very large surface area and uniform porous structure. Disadvantage of purely silica mesoporous materials, in contradiction to zeolites, is lack of ion-exchange properties and therefore deposition of catalytically active metals in the form of highly dispersed and defined species is more complex and in some cases also more expensive. The impregnation methods are not suitable for deposition of well distributed and uniform metal species. Moreover, in the case of deposition of metal species in larger amounts such methods may result in a partial clogging of pore system. Another possibility is application of methods based on grafting of metal species precursors on the silica surface followed by their thermal decomposition to uniform metal species. An example is molecular designed dispersion (MDD) method, resulting in deposition of monomeric metal species on the silica supports [23–28]. The MDD method consists of two main steps (1) reaction of metal-organic complex with silanol group of the support resulting in its anchoring on the silica surface; (2) thermal decomposition of the anchored surface complex in an oxygen containing atmosphere at elevated temperatures (calcination process), resulting in the supported catalysts with monomeric species uniformly distributed on the support surface. Another method is based on deposition of oligomeric metal species (DOMS) according to the following procedure [29–31]: (1) grafting of functionalized alkoxy silicates by their selective reaction with the surface silanol groups, optionally followed by the conversion of anchored functional groups into their anionic or cationic forms; (2) deposition of oligomeric species (e.g. oligocations) by ion-exchange method; (3) calcination of the modified silica materials to remove organic species from the samples and thermally decompose oligomeric species to stable metal oxide aggregates. The mentioned above methods allow, at least partially, control the form and dispersion of deposited metal species but are rather expensive due to multistage and complex procedures and in some cases also expensive reactants used for the modifications of the silica surface. The very promising alternative way of metal species deposition on mesoporous silicas is template ion-exchange (TIE) method [32] based on extraction of organic templates from as-synthesized mesoporous silicas (non-calcined) in a polar solvent containing metal cations. Originally, the TIE method was used for recovery of organic templates from freshly synthesized molecular silica sieves [32] but then was extended for deposition of metal species into mesoporous silica materials [33,34]. The applicability of TIE method for deposition of metal species into as-prepared mesoporous silicas depends on the nature of interactions between inorganic silica network and organic template, which can be Coulombic (S^+I^-) and hydrogen bonding (S^+I^- or $S^+X^-I^+$), where: S^0 and S^+ stand for neutral and cationic surfactant, respectively, I for the inorganic silica network, while X^- for anions [35,36]. Templates bounded to the silica framework by hydrogen bonding can be relatively easy extracted with alcohols [36], while for the removal of templates bounded to the silica network by Coulombic forces an exchange reagents are necessary [32]. It has to be noticed that such exchange is possible only for the freshly prepared mesoporous silica materials, because after attaching of protons to the surface $\equiv Si-O-$

groups (during calcination or exchange with hydronium cations) the stable $\equiv Si-OH$ silanol groups, which do not exhibit ion-exchange properties, are formed. In the case of low metal loadings it is possible to obtain catalysts with well dispersed and uniformly deposited metal species, while for the higher metal loadings also aggregated metal oxide species are formed [37,38].

The presented studies show the modified TIE method resulting in high and uniform distribution of copper species deposited on MCM-41 also in the case of the catalysts with high loading of this transition metal. MCM-41 modified with copper by the TIE was found to be active, selective and stable catalyst for the low-temperature NH₃-SCR process.

2. Experimental

2.1. Catalyst preparation

The detailed procedure used for the synthesis of MCM-41, applied as catalytic support, was presented in our previous paper [38]. A volume of 45.3 cm³ of hexadecyltrimethylammonium chloride (25% solution of HDTMACl in water, Sigma-Aldrich) and 44.0 cm³ of ammonia (25% solution of NH₃ in water, Avantor/POCH) were introduced into 525 cm³ of distilled water. The obtained mixture was intensively stirred at room temperature for 30 min., then 48.6 cm³ of tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) was dropwisely introduced and the stirring was continued for next 1 h. The solid product was separated by filtration, washed with distilled water and dried at 60 °C for 48 h.

Mesoporous MCM-41 silica was modified with copper using template-ion exchange (TIE) method. Methanol-water solutions of CuCl₂ were used for simultaneous extraction of surfactants and deposition of copper species. The solutions with different ratios of methanol and water were used. The sample of as-prepared MCM-41 (non-calcined) was introduced into a methanol-water solution of copper chloride. The obtained slurry was heated under reflux to 70 °C and intensively stirred for next 3 h. Finally, the modified silica sample was separated by filtration, washed with methanol, dried at 60 °C overnight and calcined at 550 °C for 8 h. The samples of this series are denoted as Cu-X, where X represents the volume of methanol in 100 cm³ of methanol-water solution of CuCl₂. E.g. Cu-95 is related to the sample obtained with using a methanol-water solution of CuCl₂ composed of 95 cm³ of methanol and 5 cm³ of water. The sample codes and conditions of copper deposition are presented in Table 1.

The second series of the catalysts was prepared by deposition of copper from methanol solution of CuCl₂ on as-prepared MCM-41 by TIE method. The methanol solutions with different concentration of dissolved copper chloride were used. The sample of as-prepared MCM-41(non-calcined) was introduced into a methanol solution of copper chloride. The obtained slurry was heated under reflux to 70 °C and

Table 1

The codes and conditions of copper deposition into the samples obtained by TIE and TIE-NH₃ methods.

Sample code	Solutions volumes methanol:water [cm ³ :cm ³]	Weight of non-calcined MCM-41 [g]	CuCl ₂ solution volume/concentration [cm ³]/[mmol]	Concentration of NH ₃ solution [mmol]
Cu-100	100:0	2	100/1.072	–
Cu-95	95:5	2	100/1.072	–
Cu-90	90:10	2	100/1.072	–
Cu-50	50:50	2	100/1.072	–
Cu-0	0:100	2	100/1.072	–
0.5/Cu(A)	100:0	2	100/0.536	2.114
1.1/Cu(A)	100:0	2	100/1.072	4.288
1.6/Cu(A)	100:0	2	100/1.608	6.432
2.7/Cu(A)	100:0	2	100/2.680	10.720

intensively stirred for 3 h. Then, the modified silica sample was separated by filtration, washed few times with methanol. Finally, the sample was redispersed in a water solution of ammonia (100 cm³) and intensively stirred for 1 h. The modified silica sample was separated by filtration, washed with water, dried at 60 °C overnight and calcined at 550 °C for 8 h. This modified TIE method is referred as TIE-NH₃. The samples of this series are denoted as Y/Cu(A), where Y represents the approximate concentration of CuCl₂ methanol solution, expressed in mmol, while A means that the sample was treated with ammonia solution after TIE procedure. The samples codes and conditions of copper deposition by TIE-NH₃ method are presented in Table 1.

2.2. Catalysts characterization

Textural parameters of the mesoporous silica support and its modifications with copper were determined by N₂ adsorption at −196 °C using a 3Flex (Micromeritics) automated gas adsorption system. Prior to the measurement, the sample was outgassed under vacuum at 350 °C for 24 h. The specific surface area was determined using the BET equation, while pore size was enumerated using the BJH model. The total pore volume was determined by means of the total amount of adsorbed dinitrogen at p/p₀ = 0.98.

The X-ray diffraction patterns of the studied samples were obtained with a Bruker D2 Phaser diffractometer. The measurements settings were 10 mA and 10 kV (Cu-Kα radiation, λ = 1.54056 Å). 2θ step scans of 0.02° and a counting time of 1 s per step.

The copper loading in the calcined samples were determined by electron microprobe analysis performed on a JEOL JXA 733 superprobe (electron probe microanalysis - EPMA).

The UV-vis-DR spectra of the samples were recorded to analyze the type and aggregation of deposited copper species. The measurements were performed using an Evolution 600 (Thermo) spectrophotometer operating in the range of 200–900 nm with a resolution of 2 nm.

The reducibility of copper species deposited on MCM-41 was studied by temperature-programmed reduction method with hydrogen as reductant (H₂-TPR). The measurements were carried out in a fixed-bed flow microreactor system equipped with thermal conductivity detector (Valco). The flow of gas mixture was monitored by mass flow controller (Brooks Instrument). Prior to the H₂-TPR experiments, each sample (50 mg) was outgassed in a flow of pure argon at 550 °C for 30 min. After cooling down to 100 °C the H₂-TPR runs were carried out with the linear heating rate of 10 °C min^{−1} from 100 to 900 °C in a flow of gas mixture containing 5.0 vol.% of H₂ diluted in argon (flow rate - 5 cm³ min^{−1}).

The nature and concentration of acid sites in the modified MCM-41 samples was studied by FTIR analysis of catalysts pre-adsorbed with ammonia. The samples in the form of self-supported wafers were activated under vacuum at 450 °C. FTIR spectra were recorded with Bruker Tensor 27 spectrometer, equipped with MCT detector, at spectral resolution 2 cm^{−1}. NH₃ (Linde Gas Polska, 3.5) was adsorbed in excess and consecutively evacuated at 100 °C for 10 min. All spectra were recorded at 100 °C, and normalized to a 10 mg pellet. Concentration of Cu species was calculated using the intensity of the 1620 cm^{−1} band and its absorption coefficient ε = 0.022 cm² μmol^{−1} [39].

2.3. Catalytic studies

MCM-41 modified with copper species was studied in the role of the catalysts for the DeNO_x (NH₃-SCR) process. Catalytic tests were performed in a fixed-bed quartz microreactor in the temperature range from 100 to 350 °C under atmospheric pressure. The reactant concentrations were continuously measured using a quadrupole mass spectrometer (PREVAC) connected directly to the reactor outlet. Prior to the catalytic test, 100 mg of the sample with a particle size in the range of 0.250 - 0.315 mm was outgassed in a flow of pure helium at 550 °C for 30 min. The gas mixture containing 0.25 vol.% of NO,

0.25 vol.% of NH₃ and 2.5 vol.% of O₂ diluted in pure helium was used in the catalytic tests.

For the selected sample additional catalytic stability tests in the NH₃-SCR process were done: (1) isothermal stability tests at 225 °C for 14 h, gas mixture: NO-0.25%, NH₃-0.25%, O₂-2.5%, He-97%; (2) isothermal stability tests with the periodical changes from dry (NO-0.25%, NH₃-0.25%, O₂-2.5%, He-97%) to wet (NO-0.25%, NH₃-0.25%, O₂-2.5%, H₂O-3.5%, He-93.5%) reaction mixture.

For the selected sample additional catalytic NH₃-SCR test with the increased oxygen content was done: 0.25 vol.% of NO, 0.25 vol.% of NH₃ and 5.0 vol.% of O₂ diluted in pure helium.

Moreover, the modified MCM-41 samples were tested as catalysts for the selective catalytic oxidation of NH₃ to NO and H₂O (NH₃-SCO, AMOX). Catalytic tests were performed in a fixed-bed quartz microreactor in the temperature range from 200 to 400 °C under atmospheric pressure. Similarly to previous catalytic tests, the reactant concentrations were continuously measured using a quadrupole mass spectrometer (PREVAC) connected directly to the reactor outlet. The sample of 100 mg with the particle size of 0.250 - 0.315 mm was outgassed in a flow of pure helium at 550 °C for 30 min. The gas mixture containing 0.5 vol.% of NH₃ and 2.5 vol.% of O₂ diluted in pure helium was used in the catalytic tests.

In all NH₃-SCR and AMOX tests 100 mg of catalysts was used and experiments were performed with a total flow rate of 40 cm³ min^{−1} and VHSV of about 24,000 cm³ h^{−1} g^{−1}.

3. Results and discussion

3.1. MCM-41 modified with copper – the influence of CuCl₂ solvents used on the nature of deposited copper species

Template ion-exchange method was used for simultaneous extraction of surfactants from the pore system of as-prepared MCM-41 (non-calcined) and deposition of copper species. Applied conditions of TIE method resulted only in a partial elimination of surfactants from the mesoporous silica supports and therefore in the subsequent step calcination was necessary to completely remove residual organic molecules from MCM-41. The presented results of catalysts characterization were obtained for the calcined samples.

3.1.1. Catalysts characterization

Fig. 1 shows the XRD patterns of MCM-41 modified with copper. In diffractograms of the samples three reflections, (100), (110) and (200), characteristic of typical hexagonal porous structure of MCM-41 are

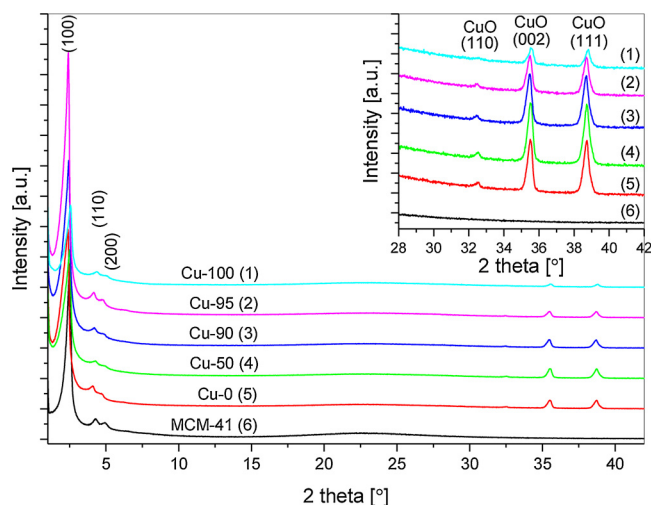


Fig. 1. Diffractograms of MCM-41 and its modifications with copper obtained by TIE method.

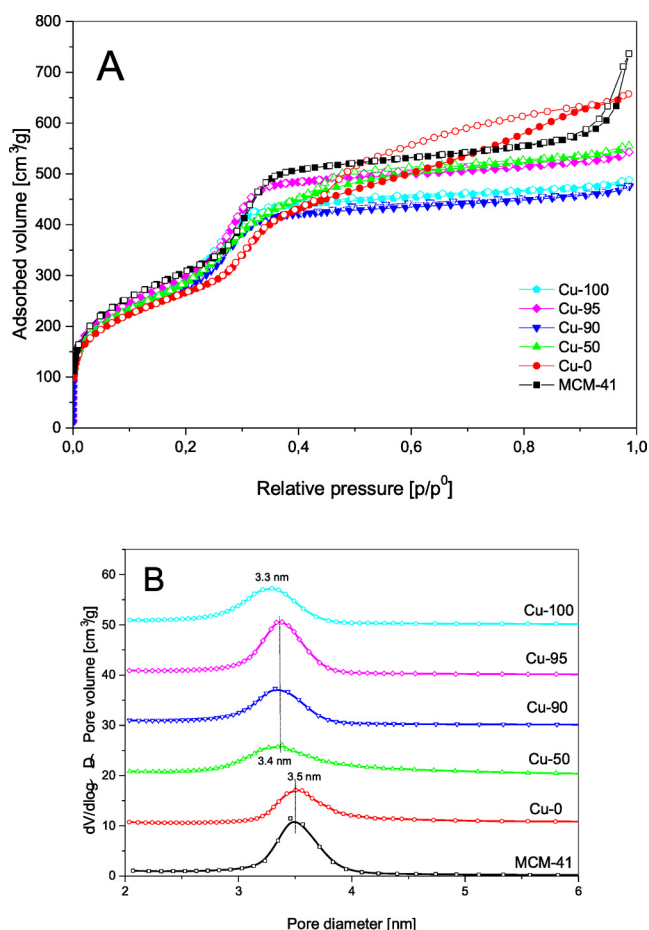


Fig. 2. N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of MCM-41 modified with copper by TIE method.

present. Lower intensity of these reflections in the case of the Cu-100 sample is possibly related to the formation of less ordered porous structure when pure methanol is used as solvent in TIE method. Moreover, it can be seen from the insert in Fig. 1, that for all samples of this series the reflections characteristic of CuO crystallites (JCPDS: 45-0937) are present in diffractograms. The average size of these crystallites, determined from X-ray diffraction line broadening, is in the range of 20–26 nm. Taking into account that the pore sizes in MCM-41 are about 3.3–3.5 nm (c.f. Fig. 2B), it can be deduced that the CuO crystallites are located outside of the pore system of the mesoporous silica supports. It should be also noted that the size of these crystallites is smaller in the case of the samples obtained with using the solutions with high content of methanol (Cu-100 and Cu-95). Thus, it seems that the rate of such CuO crystallites growth is limited in methanol in comparison to water.

Textural parameters of the samples and copper loadings are presented in Table 2, while nitrogen adsorption-desorption isotherms and profiles of pore size distributions are shown in Fig. 2. The isotherms obtained for the samples are type IV according to the IUPAC classification, which is characteristic of the mesoporous MCM-41 materials [40]. A steep increase in nitrogen uptake, observed at relative pressure p/p_0 of 0.20–0.40, is caused by capillary condensation of dinitrogen molecules inside of mesopores. The MCM-41 sample and its modifications with copper exhibit the H1 hysteresis loop typical of mesoporous materials, what indicates a narrow pore size distribution. The isotherm recorded for the Cu-MCM-41-0 sample, obtained by treatment of as-prepared mesoporous silica with an aqueous solution of CuCl₂, exhibits a sharp increase in adsorbed volume above $p/p_0 = 0.4$, characteristic of materials with high external surface area (Fig. 2A). Moreover, among

the studied silicas this sample is characterized by the lowest BET surface area and porosity. It seems that this effect is related to using of water as a solvent in TIE method. Possibly water vapour, under drying or calcination conditions, could react with the silica surface resulting in a partial hydrolysis of siloxanol bridges in freshly synthesised MCM-41. Similar effects were earlier reported in scientific literature [41]. The BET surface area and pore volume of MCM-41 decreased after deposition of copper, however these textural parameters are still very large taking into account high loading of copper (4.3–5.4 wt.%). The maximum of pore size distribution of the modified MCM-41 samples is located in the range of 3.3 to 3.5 nm and depends on the composition (CH₃OH/H₂O ratio) of solvents used in TIE method. The smallest pore size (3.3 nm) was found for the sample extracted with methanol solution of CuCl₂ (Cu-100). One of the possible explanations could be preferential deposition of copper species inside pores in the case of the Cu-100 sample and therefore decrease in pore diameter. Another explanation could be related to a partial hydrolysis of siloxanol bridges in mesoporous silica walls intensified in aqueous solvents. The largest pore diameter (3.5 nm) was determined for the sample obtained with using water as a solvent (Cu-0). This same value, 3.5 nm, was determined for pure MCM-41. Thus, it seems that in the case of this sample copper was deposited mainly on the outer surface of mesoporous silica in the form of CuO crystallites instead of deposition of this metal inside pores.

The coordination and aggregation of copper species introduced into MCM-41 was studied by UV–vis-DR spectroscopy (Fig. 3) and additionally by FTIR using NH₃ as a probe molecule (Fig. 4). In a spectrum of Cu-100 (the sample obtained with using a CuCl₂ methanol solution) two bands located at 226 and about 700 nm, related to monomeric Cu²⁺ ions interacting with oxygen of silica ($O^{2-} \rightarrow Cu^{2+}$) and to d-d transition of Cu²⁺ ions in pseudo-octahedral coordination (e.g. Cu(H₂O)₆²⁺), respectively [30,42,43], are present. An addition of small amount of water (5 vol.%) into methanolic solution of CuCl₂ during synthesis of the Cu-95 sample resulted in a decrease of the band assigned to monomeric Cu²⁺ ions (228 nm) and appearance of two new bands at about 310 and 365 nm, related to the presence of small oligomeric copper oxide species [30,42,43]. Moreover, the shoulder above 450 nm could be assigned to the formation of bulky CuO crystallites [30]. An increase of water content in a solution of CuCl₂ to 10 vol.% (Cu-90) resulted in a decrease of the intensity of the band assigned to monomeric Cu²⁺ ions (about 230 nm) and an increase of the bands related to small oligomeric copper oxide species. The shoulder above 450 nm, assigned to the presence of bulky CuO crystallites, can be also identified in the spectrum of Cu-90. In the spectrum of Cu-50, obtained by deposition of copper species with using a CuCl₂ solution consisting of 50% of water and 50% of methanol, only a very small band related to monomeric Cu²⁺ ions and broad bands assigned to oligomeric copper oxide species and bulky CuO crystallites were found. Similar results were obtained for the Cu-0 sample, obtained by deposition of copper species with using an aqueous solution of CuCl₂.

The FTIR measurements using NH₃ as a probe molecule were used for analysis of copper species dispersion on the silica surface. In a spectrum of pure MCM-41 (non-modified with copper) no bands related to ammonia molecules bounded to Lewis or Brønsted acid sites were found. Thus, all acid sites formed on the samples modified with copper were related only to the presence of transition metal species. In the FTIR spectra of all samples modified with copper the band characteristic of ammonia bounded to Lewis sites (formation of donor-acceptor bound between ammonia and copper, $NH_3 \rightarrow Cu^{n+}$) were found, while bands characteristic of ammonia bounded to Brønsted acid sites were not detected. Thus, it could be suggested that the amount of chemisorbed ammonia is proportional to the amount copper species exposed on the catalyst surface. In Fig. 4 the FTIR spectra (range characteristic for ammonia chemisorbed on Lewis sites) of the samples doped with copper are presented. It can be seen that the intensity of the band at about 1620 cm⁻¹ decreases with an increase in content of water in

Table 2
Physicochemical characteristics of the samples prepared by TIE and TIE-NH₃ methods.

Sample code	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Cu content [wt.%]/ [μmol g ⁻¹]	NH ₃ adsorption [μmol g ⁻¹]	NH ₃ /Cu [mol mol ⁻¹]	Average size of CuO crystallites [nm]	Type of copper species [mol. %]	
							Monomeric Cu ²⁺	copper oxide aggregates
MCM-41	1133	1.141	–	0	–	–	–	–
Cu-100	1073	0.756	5.4/850	811	0.95	20.10	68	32
Cu-95	1091	0.841	5.0/787	500	0.64	23.04	51	49
Cu-90	1011	0.736	5.2/819	257	0.31	24.55	23	77
Cu-50	1047	0.860	4.3/677	100	0.15	24.57	–	–
Cu-0	974	1.018	4.3/677	57	0.08	26.04	–	–
0.5/Cu(A)	1069	0.845	3.4/535	571	1.07	–	97	3
1.1/Cu(A)	1057	0.773	6.3/992	828	0.83	–	93	7
1.6/Cu(A)	964	0.769	7.4/1165	943	0.81	–	78	22
2.7/Cu(A)	960	0.739	12.9/2031	1810	0.89	–	47	53

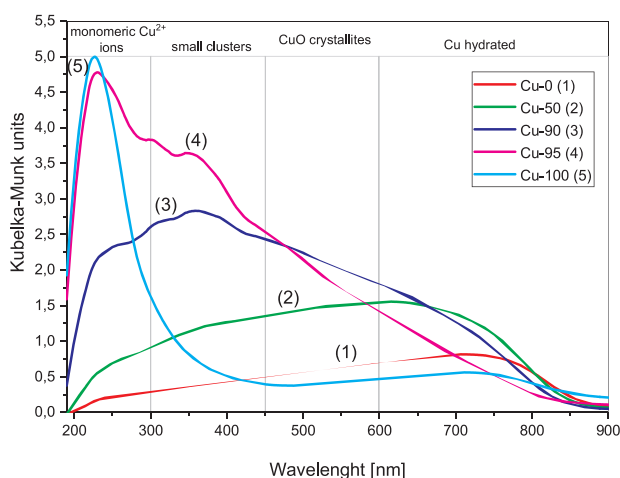


Fig. 3. UV-vis-DR spectra of MCM-41 modified with copper by TIE method.

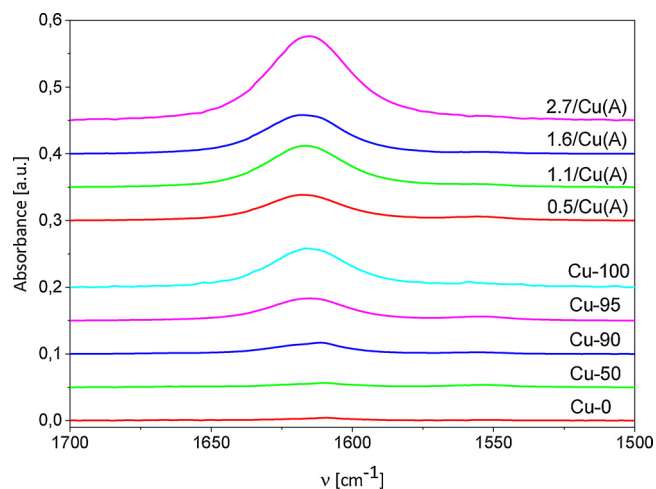


Fig. 4. FT-IR spectra of MCM-41 modified with copper by TIE and TIE-NH₃ methods adsorbed with ammonia.

methanol-water solution of CuCl₂ used for copper deposition (bottom part of Fig. 4). Thus, it could be concluded that in this same direction more aggregated copper oxide species are formed. Table 2 presents the comparison of copper loadings and surface concentrations of chemisorbed ammonia on the MCM-41 samples modified with copper by TIE method. It can be seen that in the case of the Cu-100 sample (obtained with using methanol solution of CuCl₂) the molar ratio of deposited copper and chemisorbed ammonia is about 0.95. Assuming that one

ammonia molecule is bounded to one copper cation it is suggested that nearly all copper ions are exposed on the catalyst surface and are available for the catalytic process. An increase in water content in methanol-water solution of CuCl₂ resulted in gradual decrease in the molar ratio of copper and chemisorbed ammonia. In the case of the sample obtained with using water solution of CuCl₂ (Cu-0) this ratio decreased to 0.08 (Table 2), indicating that only a very small amount of deposited copper is exposed on the catalyst surface. These results are in full agreement with UV-vis-DRS analysis of the samples, which showed increasing tendency to the formation of more aggregated copper oxide species in the case of using methanol-water solution of CuCl₂ with high content of water (c.f. Fig. 3).

The reducibility of the catalysts was studied by H₂-TPR method. The maxima present in the reduction profiles are related only to the reduction of copper species (Fig. 5). The reduction profile obtained for the Cu-100 sample consists of two peaks at 247 and about 402 °C. The low-temperature maximum is possibly assigned both to the reduction of Cu²⁺ to Cu⁰ in copper oxide species and reduction of monomeric Cu²⁺

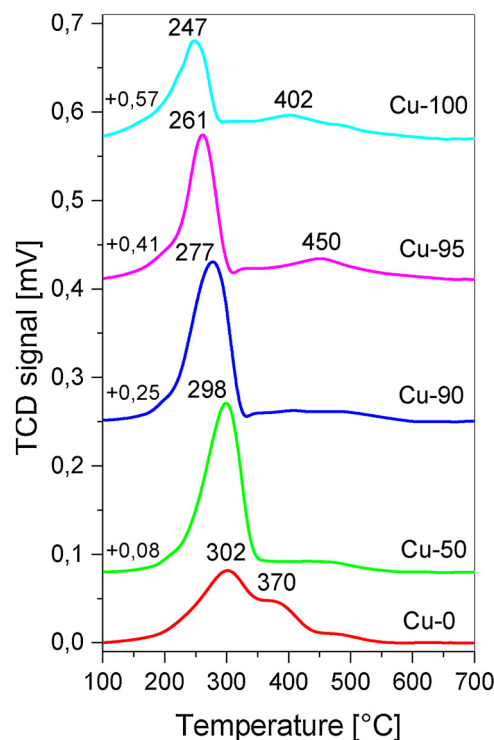


Fig. 5. Results of H₂-TPR studies of MCM-41 modified with copper by TIE method.

cations to Cu^+ [11]. While the high temperature peak is related to the reduction of monomeric Cu^+ to Cu^0 [11]. Integration of low and high-temperature peaks and comparison of their surface area leads to the conclusion that about 68% of copper in the Cu-100 sample is present in the form of monomeric cations and 32% in the form of aggregated copper oxide species. In the case of the Cu-95 catalyst 51% of copper was deposited as monomeric copper cations, while 49% of Cu is present in the form of aggregated species. While in Cu-90 only 23% of copper is present in the form of monomeric cations and 77% as aggregated copper oxide species (Table 2). In calculations of copper species contributions in the samples it was assumed that this metal is present in the calcined samples only as Cu^{2+} . Of course the presence of copper Cu^+ in modified MCM-41 cannot be fully excluded. Therefore, the presented above contributions of copper specie are only estimation. Nevertheless, this estimation clearly shows that an increase of water content in methanol-water solvent used for copper deposition by TIE method favours the formation of aggregated copper oxide species.

Another interesting effect is related to the gradual shift in a position of the low-temperature H_2 -TPR peak for the samples obtained using CuCl_2 methanol-water solvents with increasing of water content (Fig. 5). It should be noted that in this same direction increases the contribution of aggregated copper oxide species in the samples. Thus, it seems possible that such aggregated species are more difficult reducible in comparison to monomeric copper cations. In the case of the Cu-0 sample, obtained with using water solution of CuCl_2 , the reduction profile consists of two peaks located at 302 and 370 °C, which are probably assigned to the reduction of CuO aggregates of different size. Similar problem was discussed in many papers including [44]. It was suggested that an increase in the size of CuO crystallites results in a shift of the reduction peaks into higher temperatures. The other possible explanation could be partial incorporation of copper species into the silica matrix, and therefore stronger stabilization of such species against reduction.

3.1.2. Catalytic studies

The results of catalytic studies of MCM-41 modified with copper in the process of selective catalytic reduction of NO with ammonia (NH_3 -SCR) are presented in Fig. 6. It can be seen that nitrogen oxide is effectively reduced by ammonia to dinitrogen in the low-temperature range. In the case of the most active Cu-100 catalyst the NO conversion above 90%, with selectivity to N_2 in the range of 93–97%, was obtained

at temperatures 200–275 °C. Taking into account that commercial NH_3 -SCR catalysts, based on V_2O_5 - TiO_2 oxide system, effectively operate in the temperature range of 300–400 °C [4], the studied catalyst seems to be very promising for the low-temperature NO conversion. The catalysts obtained by deposition of copper with using methanol-water solutions of CuCl_2 presented lower catalytic activity. It should be noted that there is a full correlation between reducibility of the studied samples (Fig. 5) and their catalytic activity in the NH_3 -SCR process (Fig. 6). Lower temperature of the main reduction peak, the higher catalytic activity in the low-temperature NH_3 -SCR process. Thus, it seems that the redox properties of copper species deposited on MCM-41 determine their catalytic activity. As it was shown by XRD (Fig. 1), UV-vis-DRS (Fig. 3), NH_3 -FTIR (Fig. 4) and H_2 -TPR studies (Fig. 5), in a series of the studied samples the highest contribution of monomeric copper cations and lowest aggregated copper oxide species was found for the most catalytically active Cu-100 sample, obtained with using methanol solution of CuCl_2 . In the case of the samples obtained with using water containing solutions of CuCl_2 , which were less active in NH_3 -SCR, higher contribution of copper in the form of aggregated species and lower content of monomeric copper cations was detected. Thus, it supports the hypothesis that highly dispersed copper species, possibly monomeric copper cations, dispersed on the surface of MCM-41, are responsibly for high catalytic activity in the low-temperature NH_3 -SCR process. A decrease in NO conversion, observed at temperatures above 250–300 °C, is related to direct oxidation of ammonia by oxygen present in the reaction mixture. High selectivity of the NH_3 -SCR process to dinitrogen at higher temperatures shows that the main product of ammonia oxidation is N_2 . In order to verify these hypothesis additional catalytic tests of ammonia oxidation by oxygen (NH_3 -SCO, AMOX) were done for the studied catalysts (Fig. 7). It can be seen that oxidation of ammonia started at about 225–250 °C, depending on the catalyst used. The main product of ammonia oxidation is dinitrogen in the whole studies temperature range. The other product of ammonia oxidation is NO and its content increased with an increase in reaction temperature. The selectivity to NO, which is the side product of the NH_3 -SCO process, does not exceeded 10% at temperatures below 400 °C. The activity order in the process of ammonia oxidation is very similar to the activity order in NH_3 -SCR. Thus, highly dispersed copper species are probably also active in the process of ammonia oxidation to dinitrogen.

The catalytic activity of the samples in the NH_3 -SCR process is probably determined mainly by their red-ox properties. The lower

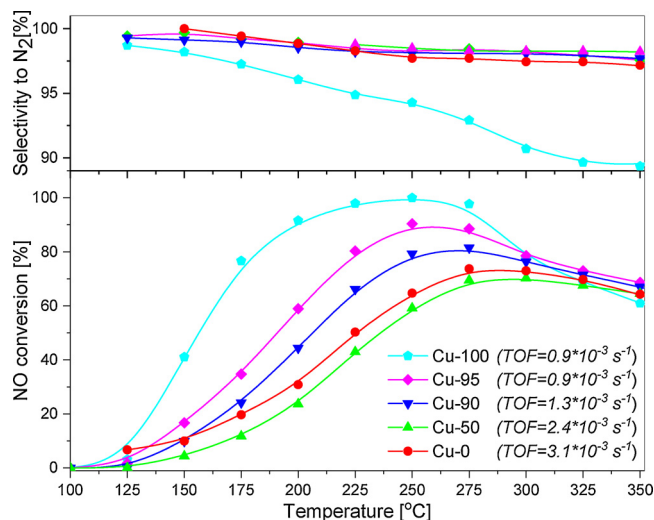


Fig. 6. Results of catalytic NH_3 -SCR tests for MCM-41 modified with copper by TIE method. Gas mixture: NO -0.25%, NH_3 -0.25%, O_2 -2.5%, He -97%, total flow rate - $40 \text{ cm}^3 \text{ min}^{-1}$, VHSV - $24,000 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$, catalyst 0.1 g. In brackets the values of turnover frequencies (TOF) determined for the reaction of NO conversion with ammonia at 200 °C are shown.

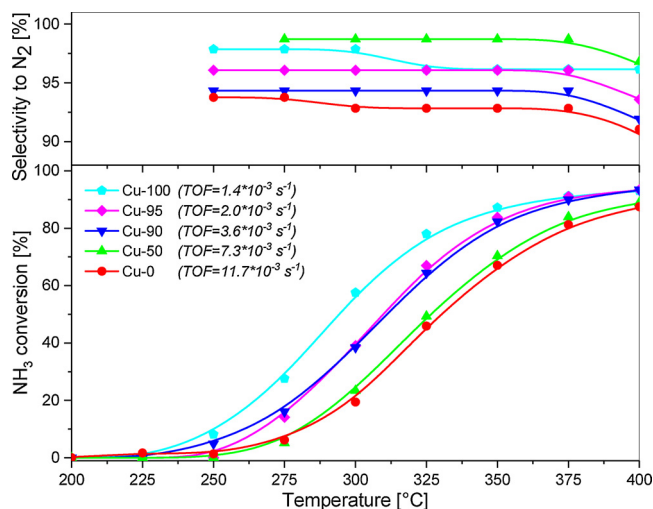


Fig. 7. Results of catalytic NH_3 -SCO (AMOX) tests for MCM-41 modified with copper by TIE method. Gas mixture: NH_3 -0.5%, O_2 -2.5%, He -97%, total flow rate - $40 \text{ cm}^3 \text{ min}^{-1}$, VHSV - $24,000 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$, catalyst 0.1 g. In brackets the values of turnover frequencies (TOF) determined for the reaction of ammonia oxidation at 325 °C are shown.

temperature of copper species reduction (H_2 -TPR, Fig. 5) means that the redox cycles may occur at temperatures lower in comparison to other samples, for which the reduction peaks are observed at higher temperatures. The results of catalytic tests in the NH_3 -SCR process and H_2 -TPR experiments support this hypothesis and show correlation between temperature of copper species reduction and low-temperature activity of the catalysts in the NH_3 -SCR process. As it was shown the correlation between reducibility of the samples and their catalytic activity in the process of selective ammonia oxidation (AMOX) is also observed. It is not surprising because also in the case of this reaction the redox properties are curtail, especially if we take into account that one on the most important mechanisms of ammonia oxidation, internal-SCR (i-SCR), reported in literature [45]. The i-SCR mechanism includes the oxidation a part of ammonia to NO in the first step, and then the reduction of NO with residual NH_3 to N_2 and H_2O in the second step. If we assume that this mechanism is also valid for the studied catalysts the obtained results, especially decrease in selectivity to N_2 and increase to NO observed at higher temperature, could be explain in the following way: (i) at lower temperatures part of ammonia is oxidized to NO and reacts with the rest of ammonia to N_2 , (ii) at higher temperatures ammonia is completely oxidized to NO and there is not enough ammonia to completely convert NO to N_2 – therefore the selectivity to dinitrogen decreases and to nitrogen oxide increases.

In Figs. 6 and 7 the turnover frequency (TOF) values, calculated for the NH_3 -SCR reaction at temperature 200 °C and for the AMOX process at 325 °C, are also presented. Temperature of 200 °C was chosen for NH_3 -SCR because, as it can be seen from Fig. 7, direct oxidation of ammonia by oxygen, which is a side reaction in NH_3 -SCR, was not occurred in this condition. Thus, the NH_3 -SCR process was not affected by the side process of ammonia oxidation. Moreover, it was assumed that the NH_3 -SCR and AMOX processes proceed through the chemisorption and activation of ammonia molecules on the catalyst surface [4,45]. The number of active sites was determined from the results of ammonia sorption measured by FTIR method (Fig. 4). It was assumed that one ammonia molecule is chemisorbed on one active copper site and all such sites are catalytically active in ammonia conversion. As it can be seen, the TOF values, determined for the NH_3 -SCR process, increased with an increase of water content in $CuCl_2$ solutions used for copper deposition (Fig. 6), what means that the samples containing more aggregated copper species possess the more catalytically active sites for NO reduction by ammonia. Of course the number of active sites in the samples containing highly dispersed copper species is much larger and therefore the overall activity of these catalysts is much higher in comparison to the catalysts with higher contribution of more aggregated copper oxide species. Similar trend in TOF changes is observed for the AMOX process (Fig. 7), however in this case the differences in the TOF values are much more significant comparing to NH_3 -SCR. Thus, it seems that in this process the aggregation of copper species is very important for the catalytic activity.

Concluding, deposition of copper in the highly dispersed form, possibly monomeric copper cations, on the MCM-41 surface results in active and selective catalysts for NH_3 -SCR. The problem with deposition of copper by TIE method is related to the formation, apart from monomeric cations, also bulky CuO crystallites less active in the NH_3 -SCR process.

3.2. MCM-41 modified with copper – the influence of post synthesis treatment with ammonia

In order to improve the efficiency of copper deposition in highly dispersed form the modified version of TIE method was applied. In this case copper was deposited on MCM-41 by TIE method using methanol solution of $CuCl_2$. After separation from the solution by filtration and washing with pure methanol, the sample was redispersed in an aqueous solution of ammonia. The final steps were filtration, drying and calcination. Detailed description of the procedures used for the sample

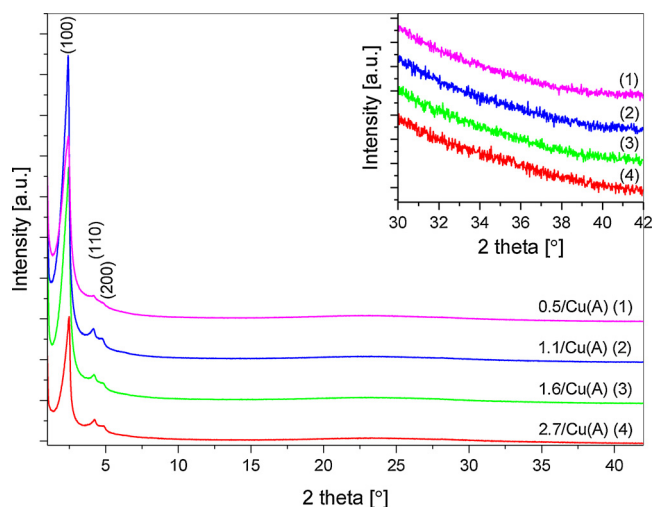


Fig. 8. Diffractograms of MCM-41 and its modifications with copper obtained by TIE- NH_3 method.

preparation is presented in *Experimental* section. The modified TIE method is referred as TIE- NH_3 . The treatment of the samples with ammonia before their calcination possibly results in the formation of the surface $(\equiv Si-O^-)_2[Cu(NH_3)_n]^{2+}$ complexes, which should be more resistant for sintering during the calcination process and therefore it is expected that the formation of aggregated CuO crystallites should be limited in this case.

3.2.1. Catalysts characterization

Fig. 8 presents diffractograms of the samples obtained by TIE- NH_3 procedure. In diffractograms the reflections (100), (110) and (200), characteristic of hexagonal porous structure of MCM-41, are present. However, the intensity of these reflections, especially (100) recorded for 0.5/Cu(A) and 2.7/Cu(A), so the samples with the lowest and the highest copper loadings are reduced in comparison to other catalysts of this series. In the case of 0.5/Cu(A) the TIE- NH_3 method resulted in extraction of smaller amount of organic surfactants in comparison to other samples of this series. Thus, during the calcination of 0.5/Cu(A) directly after TIE- NH_3 the expected overheating of the sample, due to exothermal incineration of residual surfactants, is more significant than for the other samples of this series. Ammonia (complexing agent of Cu species) and water (used as ammonia solvent) released during calcination may react with silica (e.g. hydrolysis of siloxanol bridges in the silica walls) at elevated temperatures generated by exothermal burning of residual surfactants. Of course this effect is present for all the samples of this series but for 0.5/Cu(A) is expected to be intensified due to the higher content of residual surfactants.

On the other side the sample 2.7/Cu(A), which contained much smaller amounts of residual surfactants in comparison to other samples of this series but much higher content of ammonia complexing deposited copper species. Thus, it is possible that during calcination, ammonia released in much higher amounts than in other samples of this series, may react with the silica walls resulting in their partial degradation.

In contradiction to the first series of the samples the reflections characteristic of CuO crystallites are not present in diffractograms of the samples obtained by the TIE- NH_3 method (Fig. 8, insert). Thus, post-treatment of the samples with ammonia protects the highly dispersed copper species against aggregation.

Textural parameters and copper content is presented in Table 2. It should be noted that introduction as large content of copper as 12.9 wt. %, 2.7/Cu(A), did not resulted in the formation of bulky CuO crystallites. The surface area and pore volume of the samples obtained by TIE- NH_3 method slightly decreased with an increase in copper loading.

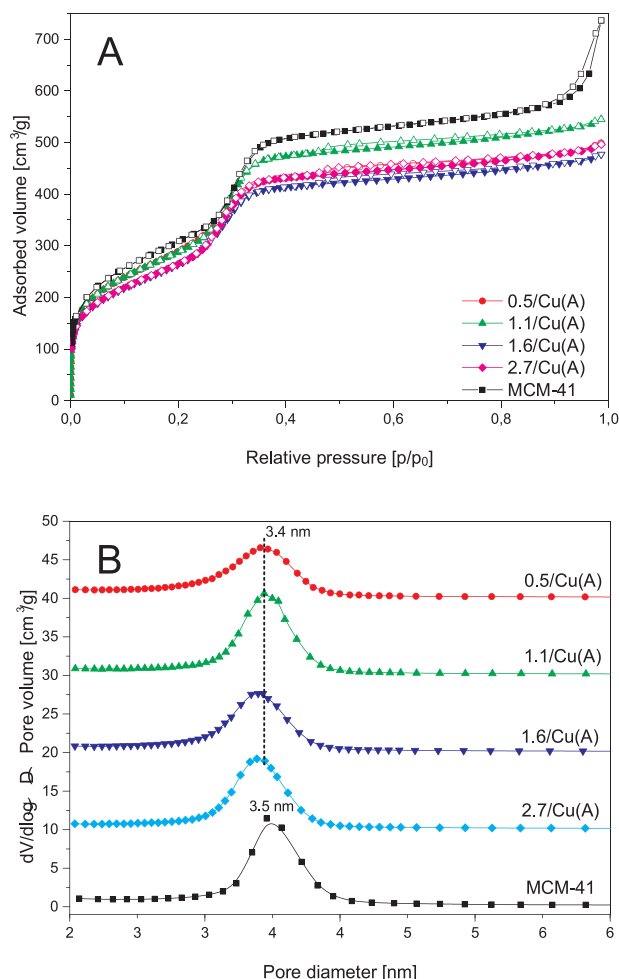


Fig. 9. N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of MCM-41 modified with copper by TIE-NH₃ method.

N₂ adsorption-desorption isotherms and profiles of pore size distributions of the samples obtained by TIE-NH₃ method are shown in Fig. 9. The isotherms of all the samples of this series are type IV according to the IUPAC classification (Fig. 8A), which is characteristic of mesoporous MCM-41 materials [38]. A steep increase in dinitrogen uptake, observed at relative pressure p/p_0 of 0.20–0.40, is caused by capillary condensation of nitrogen molecules inside mesopores. The samples exhibit the H1 hysteresis loop typical of mesoporous materials with a narrow pore size distribution. As it can be seen in Fig. 9B, the maxima of pore size distribution for all samples obtained by TIE-NH₃ method are relatively narrow and centred at about 3.4 nm, what in comparison to the size of pores in MCM-41 (3.5 nm) may suggest deposition of copper species inside pores of the silica support.

The coordination and aggregation of copper species introduced into MCM-41 by TIE-NH₃ method was analysed by UV-vis-DR spectroscopy (Fig. 10). The spectra obtained for all samples of this series consist of two bands located at 220–227 and about 780 nm, related to monomeric Cu²⁺ ions interacting with oxygen of silica ($O^{2-} \rightarrow Cu^{2+}$) and to d-d transition of Cu²⁺ ions in pseudo-octahedral coordination (e.g. Cu (H_2O)₆²⁺), respectively [30,42,43]. The shoulder in the range of 280–410 nm is related to the presence of small oligomeric copper oxide species [30]. Bands assigned to bulky copper oxides species were not found in the spectra of the studied samples. The intensities of the bands increase with an increase in copper loading. Thus, the UV-vis-DRS analysis of MCM-41 modified with copper by TIE-NH₃ method proves deposition of this metal in the form of highly dispersed species, also in the samples with high copper loadings.

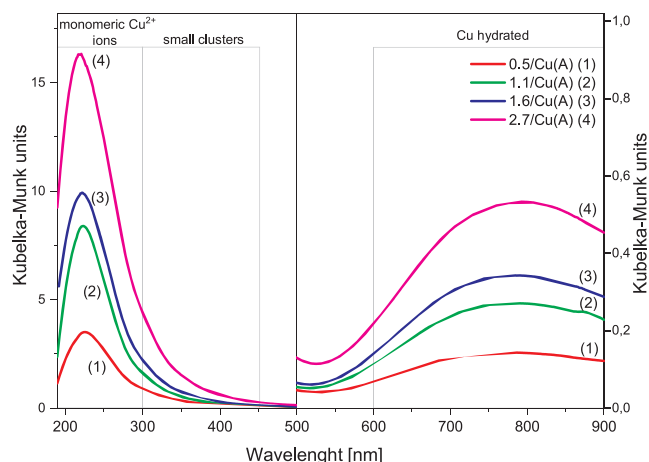


Fig. 10. UV-vis-DR spectra of MCM-41 modified with copper by TIE-NH₃ method.

Similarly to the previous series of the samples, also for the catalysts obtained by TIE-NH₃ method, the surface availability of copper was estimated by FTIR measurements of the samples pre-adsorbed with ammonia. Also in this case only chemisorption of ammonia on Lewis acid sites (formation of donor-acceptor bound between ammonia and copper, $NH_3 \rightarrow Cu^{n+}$) was detected. Fig. 4 presents the FTIR spectra (range characteristic for ammonia chemisorbed on Lewis sites) of the samples doped with copper. It can be seen that the intensity of the band at about 1620 cm⁻¹ increases with an increase in copper loading (a series of the samples obtained by TIE-NH₃ method is presented in upper part of Fig. 4). Table 2 shows the comparison of copper loadings and surface concentrations of chemisorbed ammonia on the MCM-41 samples modified with copper by TIE-NH₃ method. It can be seen that in the case of the 0.5/Cu(A) sample, so the catalyst with the lowest copper content in this series, the molar ratio of chemisorbed ammonia and copper content is close to 1. Thus, assuming that one ammonia molecule is chemisorbed on one copper cation, it could be suggested that all copper species are exposed in the silica surface and available for catalysis. An increase in copper loading results in a decrease of the ammonia to copper ratio, however this value did not drop below 0.8. These results clearly show that application of the TIE-NH₃ method results in better dispersion of copper on the MCM-41 surface in comparison to the classical TIE procedure.

The H₂-TPR profiles of the samples obtained by TIE-NH₃ method are shown in Fig. 11. The reduction profile of the 0.5/Cu(A) sample consists of two peaks at 230 and about 465 °C. The low-temperature maximum is related both to the reduction of Cu²⁺ to Cu⁰ in copper oxide species and reduction of monomeric Cu²⁺ cations to Cu⁺ [11]. While the high temperature peak is assigned to the reduction of monomeric Cu⁺ to Cu⁰ [11]. An increase in copper loadings resulted in a shift of the low-temperature peak from 230 to 235 °C. More significant shift was observed for the high-temperature reduction peak. Integration of low- and high-temperature peaks and comparison of their surface area leads to the estimation of contribution of copper introduced into MCM-41 in the form of monomeric copper cations and small oligomeric copper oxide species. Results of this analysis are compared in Table 2. In calculations it was assumed that copper in the outgassed samples is present only as Cu²⁺. It can be seen that the contribution of copper in the form of oligomeric copper oxide species increases with an increase in loading of this metal. It should be noted that crystallites of CuO were not detected in XRD studies (Fig. 8), thus the aggregated species are probably small oligomeric species (below detection level of XRD method). This hypothesis is proved by the results of UV-vis-DRS studies (Fig. 10), which have shown the presence of the intensive band at about 220–230 nm related the presence of monomeric copper cations and small shoulder in the range of 300–450 nm related to such small oligomeric copper

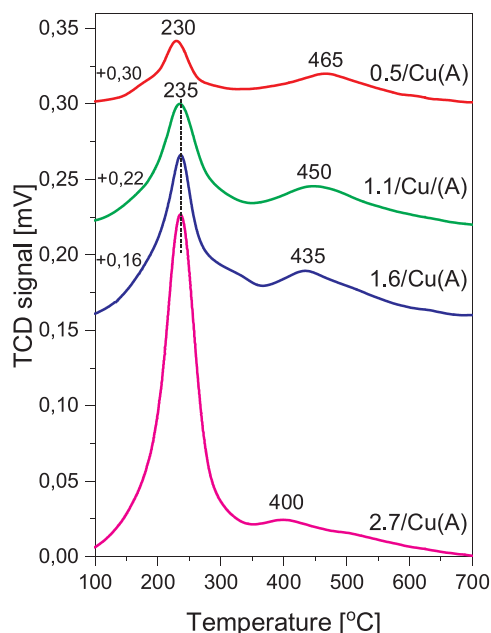


Fig. 11. Results of H_2 -TPR studies of MCM-41 modified with copper by TIE- NH_3 method.

species [30,42,43]. The bands related to bulky CuO oxide species were not found in the UV–vis-DR spectra recorded for the studied samples of TIE- NH_3 series.

3.2.2. Catalytic studies

Results of catalytic tests of the samples obtained by TIE- NH_3 method in the NH_3 -SCR process are shown in Fig. 12. It can be seen that, similarly to the previous series of the samples, also in this case the studied catalysts effectively operate in the low-temperature NH_3 -SCR process. The NO reduction started at about 100 °C and sharply increased with an increase in reaction temperature to 250–275 °C. At higher temperatures a decrease in NO conversion, due to the side process of direct oxidation of ammonia by oxygen present in the reaction mixture, was observed. Catalytic activity in the NH_3 -SCR process increases with

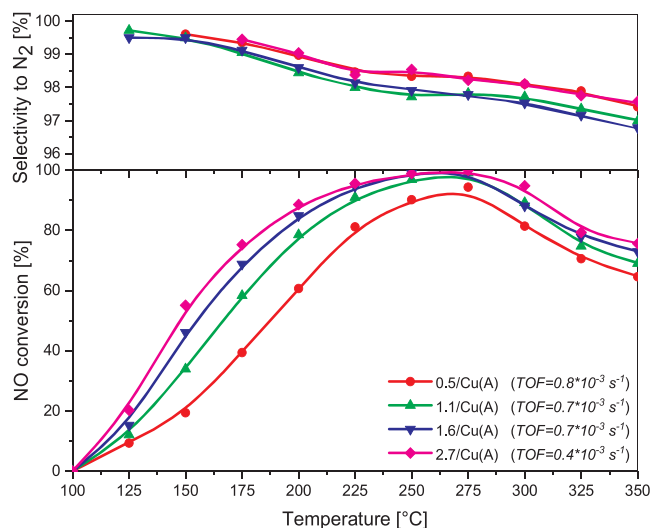


Fig. 12. Results of catalytic NH_3 -SCR tests for MCM-41 modified with copper by TIE- NH_3 method. Gas mixture: NO -0.25%, NH_3 -0.25%, O_2 -2.5%, He -97%, total flow rate - $40\text{ cm}^3\text{ min}^{-1}$, VHSV - $24,000\text{ cm}^3\text{ h}^{-1}\text{ g}^{-1}$, catalyst 0.1 g. In brackets the values of turnover frequencies (TOF) determined for the reaction of NO conversion with ammonia at 200 °C are shown.

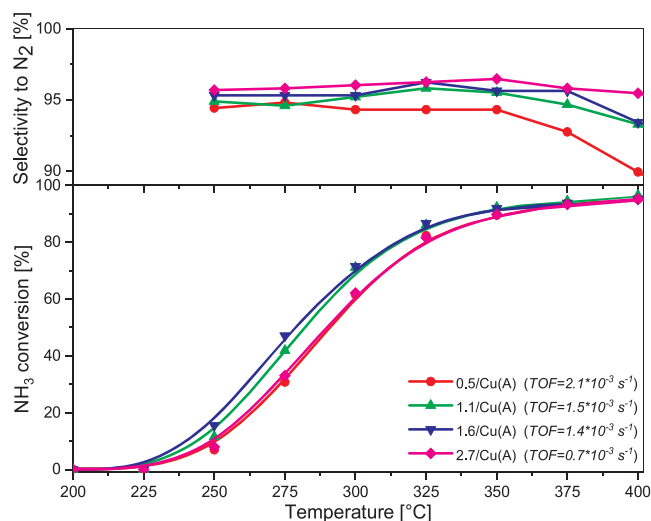


Fig. 13. Results of catalytic NH_3 -SCO (AMOX) tests for MCM-41 modified with copper by TIE- NH_3 method. Gas mixture: NH_3 -0.5%, O_2 -2.5%, He -97%, total flow rate - $40\text{ cm}^3\text{ min}^{-1}$, VHSV - $24,000\text{ cm}^3\text{ h}^{-1}\text{ g}^{-1}$, catalyst 0.1 g. In brackets the values of turnover frequencies (TOF) determined for the reaction of ammonia oxidation at 325 °C are shown.

an increase in copper loading in the samples. In the case of the most active catalyst, 0.5/Cu(A), the NO conversion above 90% was achieved in the temperature range of 200–300 °C. So, in the range broader by about 25 °C in comparison to the most active catalyst of the previous series (Cu-100). It should be noted that the catalysts obtained by TIE- NH_3 method were highly selective to dinitrogen (above 97%) in the whole studied temperature range. Thus, it could be supposed that also the side process of direct ammonia oxidation at higher temperatures should result mainly in the formation of dinitrogen. To verify this hypothesis the catalysts obtained by TIE- NH_3 method were additionally tested in the process of ammonia oxidation (NH_3 -SCO, AMOX). As can be seen (Fig. 13) in the case of all studied catalysts, the main product of ammonia oxidation is N_2 . The second product of ammonia oxidation is NO and its content increased with an increase in reaction temperature. The selectivity to NO did not exceeded 10% at temperatures below 400 °C. Comparison of the results of ammonia oxidation presented in Figs. 7 and 13 shows that the samples obtained by TIE- NH_3 method are slightly more catalytically active in this process.

In Figs. 12 and 13, turnover frequency (TOF) values calculated for the NH_3 -SCR and AMOX reactions are also presented. Similarly to a previous series of the samples the TOF values were determined for the reactions conducted at 200 °C for AMOX and 325 °C for NH_3 -SCR. Moreover, it was assumed that the NH_3 -SCR and AMOX processes proceed through the chemisorption and activation of ammonia molecules on the catalyst surface [4,45]. It can be seen that the TOF values, determined for the NH_3 -SCR process, were nearly stable for the samples with lower copper loadings and significantly decreased for the sample with the highest copper loading, 2.7Cu(A), (Fig. 12). Thus, it seems that small oligomeric copper oxide species are less catalytically active in NH_3 -SCR in comparison to monomeric copper cations. Of course, the number of active sites in the 2.7Cu(A) sample is much larger and therefore the overall activity of this catalyst is higher in comparison to the catalysts with the lower copper loadings. In the case of AMOX (Fig. 13), a decrease in the TOF values is observed for the samples with increasing copper loadings. It should be noted that the changes of the TOF values are significantly lower in comparison to a previous series of the samples (Fig. 7). Thus, it seems that highly dispersed copper species (monomeric cations and small oligomeric copper oxides species) are less catalytically active in the AMOX process in comparison to more aggregated copper species.

Comparison activity of the catalysts of both series but containing

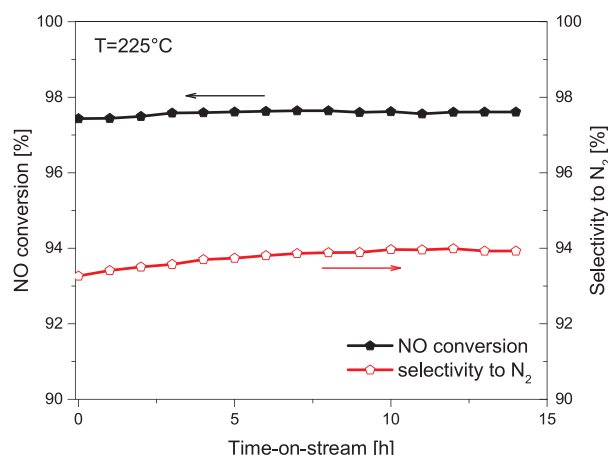


Fig. 14. Stability NH₃-SCR catalytic test for the Cu-100 sample at 225 °C. Gas mixture: NO-0.25%, NH₃-0.25%, O₂-2.5%, He-97%, total flow rate - 40 cm³ min⁻¹, VHSV -24,000 cm³ h⁻¹ g⁻¹, catalyst 0.1 g.

similar amounts of deposited copper, Cu-100 (5.4 wt.% Cu) and 1.1/Cu (A) (6.3 wt.% Cu) shows slightly higher activity in the NH₃-SCR process of the former catalyst but at higher temperatures the side process of ammonia oxidation was less intensive in the presence of the catalyst obtained by TIE-NH₃ method. Also selectivity to dinitrogen was higher in the case of this catalyst.

The results of isothermal (225 °C) stability test in the NH₃-SCR process for the Cu-100 catalyst are presented in Fig. 14. It can be seen that both NO conversion and selectivity to N₂ were not significantly changed during 14 h of the catalytic test. Moreover, the catalytic isothermal (225 °C) test showing the influence of water vapour on the catalytic performance of the Cu-100 sample in the NH₃-SCR process is presented in Fig. 15. Water vapour was periodically, in 30 min. intervals, added into reaction mixture. It can be seen that after first exchange from dry to wet reaction mixture the NO conversion dropped by about 10% from 97 to 87%, but in the next step of exchange from wet to dry reaction mixture the NO conversion was partially recovered. Thus, it seems that water vapour resulted in a partial deactivation of the studied catalyst. However, an increase in the NO conversion after exchange from wet to dry reaction mixtures suggests that there is a completion of ammonia and water for the same adsorption sites and therefore partial recovery of the catalyst activity was observed. Similar

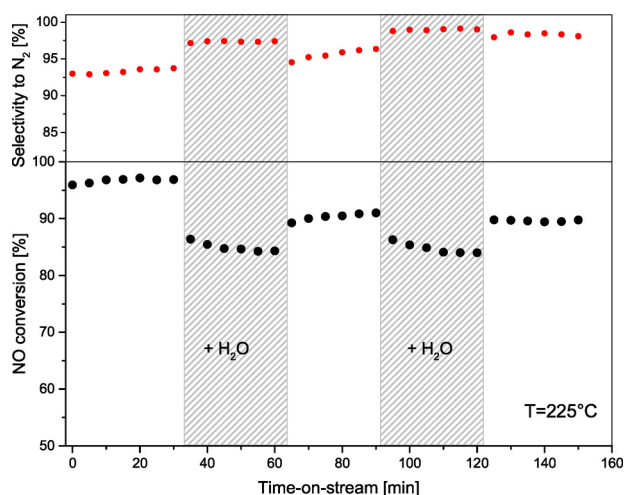


Fig. 15. Stability NH₃-SCR catalytic test with the periodical exchange from dry (NO-0.25%, NH₃-0.25%, O₂-2.5%, He-97%) to wet reaction mixture for the Cu-100 sample at 225 °C. Gas mixture: NO-0.25%, NH₃-0.25%, O₂-2.5%, He-97%, total flow rate - 40 cm³ min⁻¹, VHSV -24,000 cm³ h⁻¹ g⁻¹, catalyst 0.1 g.

effect was observed in our previous studies for montmorillonites intercalated with silica-titania pillars [46]. It should be also noted that in the next cycle of exchange from wet to dry gas mixture the full recovery of the NO conversion was observed. Moreover, selectivity to N₂ in wet atmosphere was slightly higher in comparison to dry conditions.

The catalytic test performed for the Cu-100 samples with the increased content of oxygen has not result insignificant changes in the efficiency of the NH₃-SCR process (supplementary materials).

4. Conclusions

MCM-41 was doped with copper by template ion-exchange method (TIE) using menthol-water solutions of CuCl₂. It was shown that an increase of water content in such solutions results in the intensified formation of aggregated CuO crystallites. Therefore, the lowest contribution of copper in the form of such crystallites was found for the sample obtained with using a purely methanol solution of CuCl₂. This catalyst was also the most active in the low-temperature NH₃-SCR process and therefore a very important role in catalytic process was attributed to the highly dispersed copper species (monomeric cations and small oligomeric metal oxide species) deposited on the MCM-41 surface. In order to increase the contribution of copper in the form of highly dispersed species the second series of the samples was prepared by the modified TIE method. In this case the as-prepared samples, after extraction with methanol solution of CuCl₂, were treated with an aqueous solution of ammonia to complexate deposited copper cations (TIE-NH₃). It was shown that calcination of such samples results in highly dispersed copper species without formation of bulky CuO crystallites, even in the sample containing as high copper loading as 12.9 wt.%. The samples obtained by TIE-NH₃ method were catalytically active in the low-temperature NH₃-SCR process, however their catalytic performance depended on the copper loading. In the case of the most active catalyst of this series the NO conversion above 90%, with selectivity to N₂ above 97%, was obtained in the range of 200–300 °C. Comparison of the catalysts obtained by TIE (Cu-100) and TIE-NH₃ methods (1.1/Cu(A)) with similar loadings of copper (5.4 and 6.3 wt.% Cu, respectively) shows slightly higher activity in the NH₃-SCR process of the former catalyst but at higher temperatures the side process of ammonia oxidation was less intensive in the presence of the catalyst obtained by TIE-NH₃ method. Thus, it seems that apart from highly dispersed copper species also coexistence of small amounts of aggregated CuO crystallites is important for the low-temperature NH₃-SCR process. On the other side such crystallites decreases selectivity to dinitrogen and therefore also the efficiency of the NH₃-SCR process at higher temperatures. In the stability test performed for the Cu-100 catalyst any significant changes in the NO conversion and selectivity to N₂ was observed during 14 h, while the studies with the reaction mixture containing H₂O showed small deactivation of the catalyst in the NH₃-SCR process, which is partially reversible after exchange from wet to dry reaction mixture.

The studied catalysts, obtained by deposition of copper into MCM-41 by TIE and TIE-NH₃ methods seem to be very promising for the low-temperature NH₃-SCR process. High catalytic activity of these catalysts is probably attributed to deposition of large number of dispersed copper species on a very high surface area of the silica support, with a relatively large pores allowing fast internal diffusion of reactants.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.06.052>.

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